

Item 0001AC, Final Technical Report

July 15, 2005

Contract No. FA9550-04-C-0119
An STTR contract of Fluorochem, Inc., in collaboration with SRI

All-Nitrogen Compounds as High Energy Density Materials

To:

AFOSR/NL (Dr. Michael R. Berman)
4015 Wilson Blvd, Room 713
Arlington, VA 22203-1954

From:

Fluorochem, Inc.
680 South Ayon Avenue
Azusa, CA 91702

Contributors

Fluorochem, Inc.: Kurt Baum, Rodney L. Willer
SRI: Jeffrey Bottaro, Mark Petrie, Paul Penwell, Allen Dodge, Ripu Malhotra

20050728 096

0305

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Office of Management and Budget, Paperwork Reduction Project, Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	15 Jul 05	FINAL	
4. TITLE AND SUBTITLE All-Nitrogen Compounds as High Energy Density Materials			5. FUNDING NUMBERS FA9550-04-C-0119
6. AUTHOR(S) Baum, Kurt			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Flurochem, Inc. 680 South Ayon Ave. Azusa, CA 22203-1954			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 875 North Randolph St. Suite 325, Rm 3112 Arlington, VA 22203			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) There is a continuing need for safe, versatile rocket propellants, which are stable, nonvolatile, energetic, and easily demilitarized. Ionic liquids constitute a research area that is little explored for propellant ingredients and provides potential to meet these requirements. Enhanced dissolving power, density and compatibilities with a wide range of propellant ingredients make ionic liquids a very attractive class of materials for advanced state-of-the-art propulsion systems. The extreme polarity of these unique liquid media opens the door to novel burn-rate and ballistic attenuation technologies. The objective of this Phase I SBIR program is to canvass and select the most promising candidates for development of energetic ionic liquid and other high-nitrogen energetic ingredients.			
14. SUBJECT TERMS		15. NUMBER OF PAGES 4	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

7-25-05

INTRODUCTION

There is a continuing need for safe, versatile rocket propellants, which are stable, nonvolatile, energetic, and easily demilitarized. Ionic liquids constitute a research area that is little explored for propellant ingredients and provides potential to meet these requirements. Enhanced dissolving power, density and compatibilities with a wide range of propellant ingredients make ionic liquids a very attractive class of materials for advanced state-of-the-art propulsion systems. The extreme polarity of these unique liquid media opens the door to novel burn-rate and ballistic attenuation technologies. The objective of this Phase I SBIR program is to canvass and select the most promising candidates for development of energetic ionic liquid and other high-nitrogen energetic ingredients.

DISCUSSION

The following categories of materials were targeted as potential potential components of ionic liquids with a broad liquidus

CATIONS

- a. 1, 3 dialkyl-1,2,3-triazolium salts
- b. 1,3 dimethoxy-1,2,3-triazolium salts
- c. 1-fluoro-3-methoxy 1,2,3-triazolium salts
- d. 1,3 or 1,4-dialkyl tetrozolium salts
- e. 1,3 or 1,4-dimethoxy tetrozolium salts
- f. 1-fluoro-3-methoxy or 1-fluoro-4-methoxy tetrazolium salts
- g. 2-azido-ethyl hydrazinium salts
- h. 2-azido-ethyl-hydroxylammonium salts
- i. 2-azidoethyl ammonium salts
- j. difluoroamino tetrazoles in alkylated or aminated cationic form
- k. dimethoxy ammonium
- l. N-fluoro-N-alkylimmonium

ANIONS

- a. 5-nitrotetrazole-2-oxides
- b. dinitramides

- c. trinitromethyl anions
- d. cyano dinitromethyl anions
- e. azido ethyl nitramine anions
- f. azidomethyl dinitromethanes
- g. trinitroethyl nitramine anions
- h. nitro triazoles and their N-oxides
- i. C-(trifluoro methyl) tetrazoles and their N-oxides
- j. C-(trifluoro methyl) triazoles and their N-oxides
- k. C-(difluoroamino) triazoles and tetrazoles and their N-oxides in anionic form
- l. C-(Pentafluorosulfuranyl) triazoles and tetrazoles and their N-oxides in anionic form
- m. perbromate

IONIC LIQUIDS AND LOW-MELTING SOLIDS SYNTHESIZED ON THIS PROGRAM

The following liquid ionic/low melting salts were prepared by conventional ion exchange techniques employing the corresponding ionic components.:

- 1. methoxy ammonium dinitramide
- 2. azidoethyl hydrazinium dinitramide
- 3. 1-methyl-3-ethyl imidazolium 5-nitrotetrazole-2-oxide
- 4. 1-methoxy-3-methyl tetrazolium fluoroborate
- 5. 1,4 dimethyl tetrazolium dinitramide
- 6. 1,3 dimethyl 1,2,3-tetrazolium dinitramide
- 7. tris(nitrato ethyl) methyl ammonium dinitramide
- 8. acetyl choline dinitramide
- 9. 1,4 dimethyl 1,2,4-triazolium dinitramide

ALL OF THESE MATERIALS HAD ACCEPTABLE THERMAL STABILITY (DSC
≥130°C

One material which had an excessively high melting point ($>75^{\circ}\text{C}$) was 2-azidoethyl hydrazinium azide, a possible monopropellant. Azidoethyl ammonium nitrate also melted too high to be an ideal ionic liquid.

SYNTHONS AND BUILDING BLOCKS ASSEMBLED

The following useful synthons for the assembly of liquid-promoting anions and cations were prepared:

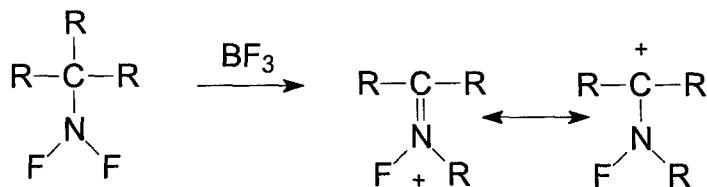
1. 2-Azidoethyl tosylate (enables synthesis of azidoethyl amines, hydrazines, and hydroxylamines, all of which can be converted to low-melting salts)
2. Propylenimine was found to react cleanly with HN_3 to give 1-azido-2-amino propane. This compound can be converted directly to salts, or it can be N-nitrated to give 1-azido-2-propyl nitramine, which can be used as the acidic component in salt formation. This reaction with ethylenimine is expected to give 2-azidoethylamine.
3. N-Amination of a variety of triazoles and tetrazoles with O-(toluenesulfonyl) hydroxylamine to give various N-amino azolium salts was carried out. Product characterization is incomplete..

CONCLUSIONS

Preliminary work has been carried out to demonstrate the practicality of novel classes of ionic liquids.

1. 2-Nitroethyl ammonium salts, especially the dinitramide salts, which by virtue of their exceptional charge delocalization and concomitant reduction in solvation energy, display remarkably low melting points while retaining acceptable stability at room temperature. Their enthalpy and oxygen balance is favorable.

2. The dialkyl imidazolium salts of the 5-nitrotetrazole-2-oxide anion are low melting or liquid. A variety of ionic liquids are thus available based on 5-nitrotetrazole-2-oxide anion, easily accessible by peroxyulfate oxidation of 5-nitrotetrazole.
3. Azidoethanol, azidoethyltosylate, and 1-azido-2-aminopropane, potentially available on an industrial scale, enable a large array of energetic ionic liquids to be made. Among these are the azidoethyl ammonium salts, azidopropyl nitramine salts, and azidoethyl derivatives of heterocyclic cations.
4. Because of their extensive charge delocalization, dinitramide anions generally give low-melting salts.
5. N-Fluoroimmonium salts, readily prepared by the rearrangement of alkylidifluoramines with Lewis acids, can potentially provide a cation base for NF-containing ionic liquids. Screening of alkylidifluoramines with various substrates would give an indication of liquidus of this class of ionic liquids.



6. The use of perbromate as an ionic liquid component would require theoretical performance studies. Consideration of perbromate salts as solid propellant components, e.g., ammonium perbromate as a replacement for AP, would depend on theoretical performance and environmental evaluation.